

Preliminary Survey of Ambient Air Levels
of PAH in Winnipeg

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Air Standards and Studies
Report No. 84-3

Bennett, M., 1984, Preliminary Survey of Ambient Air Levels of PAH in Winnipeg, Department of Environment and Workplace Safety and Health, Air Standards and Studies Section, Report No. 84-3. pp. 22.

Abstract

A preliminary study was undertaken to determine if polynuclear aromatic hydrocarbons (PAH) are present in the ambient air of Winnipeg. Sampling was performed at 3 urban Winnipeg stations and one rural background station using high-volume particulate samplers equipped with glass fibre filters. Samples were obtained over 24-hour periods every 6th day during a five week period in late February and March 1984.

No quantification of PAH was possible as all levels, with one exception, were below analytical detection limits. Despite the wide spread employment of the method of high-volume air sampling for PAH, this method may not be appropriate due to poor collection efficiencies and the inability to collect gaseous compounds. Improved lower analytical detection limits may also be necessary.

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1. INTRODUCTION

Due to the wide spread use of wood combustion as a source of, or supplement to, residential heating, a preliminary study was undertaken to investigate if this phenomenon was having an impact on urban air quality in Winnipeg. Sampling was conducted for polynuclear aromatic hydrocarbons (PAH) using high-volume particulate samplers at 3 urban Winnipeg sites and one rural "background" station. Site descriptions are given in the Procedures section. The investigation was performed over a 4 week period from February 24 to March 25, 1984 with 24-hour samples obtained every sixth day.

Polynuclear aromatic hydrocarbons (PAH) constitute a significant component of both the particulate matter and gaseous emissions in wood smoke. In total there are in excess of 50 compounds which may be categorized as PAH. These compounds are routinely a by-product of incomplete combustion or pyrolysis of flammable hydrocarbons.¹ Incomplete combustion is that which is limited by available oxygen. The temperature of combustion is also an important factor in determining which PAH compounds will be generated.² Particulate PAH compounds are primarily in the respirable size range³ (<10 μ m), having an aerodynamic size range conducive to deposition in the alveolar area of the lungs.

The specific PAH components of this study were the following chemicals:

- 1) Fluorene $C_{13}H_{10}$ Molecular Weight = 166.2
- 2) Fluoranthene $C_{16}H_{10}$ M.W. = 202.3
- 3) Benzo[a]pyrene) $C_{20}H_{12}$ M.W. = 252.3 (also called 3,4-Benzopyrene)
- 4) Phenanthrene $C_{14}H_{10}$ M.W. = 178.2
- 5) Chrysene* $C_{18}H_{12}$ M.W. = 228.3 (also called 1,2-Benzophenanthrene) and Triphenylene* $C_{18}H_{12}$ M.W. = 228.3 (also called 9,10-Benzophenanthrene)
- 6) Pyrene $C_{16}H_{10}$ M.W. = 202.1

Quantitatively the above compounds constitute approximately 43% of the total PAH emissions from wood stoves and 31% from fireplaces.⁴ These estimates are based on the following observed emission factors⁵; 0.41 grams of total PAH per kilogram of wood for stoves and 0.063 grams per kg for fireplaces. As mentioned, these values are estimates and may vary depending on the temperature of combustion, the type of wood burning devise and the type of wood.

Evidence provided by various researchers suggests that some polynuclear aromatic hydrocarbons are toxic and represent priority pollutants.^{6,7,8,9,10} Some are strongly carcinogenic (eg. benzo[a]pyrene) or are co-carcinogens (fluoranthene and pyrene). Others represent cilia toxic, mucus coagulating agents or respiratory irritants.

* As Chrysene and Triphenylene are isomers they are indistinguishable from one another by our analytical methods.

Wood burning emissions are customarily much greater in winter (along with the combustion of other fossil fuels such as oil and coal) and it was for this reason that the project was conducted in February and March. Other studies have noted significant increases in wintertime PAH concentrations from a variety of sources.^{10,12,13}

The objectives of this study were:

- 1) To determine (using high-volume particulate sampling) if detectable quantities of polynuclear aromatic hydrocarbons were routinely present in urban ambient air.
- 2) To render an assessment of PAH impact on air quality, if they are present, by comparing levels with those found in other jurisdictions.
- 3) To try to quantify the difference in concentrations, first between a rural background station and the urban monitoring sites, and secondly, between different urban environments such as residential and downtown commercial areas.
- 4) To obtain information regarding the size of PAH compounds (if present) using a 10 μ m size selective sampler at the downtown station. This sampler selectively samples particulate in the respirable size range (10 μ m or less).

2. PROCEDURES

Sampling was conducted using standard high-volume particulate samplers with glass fibre filters. This sampling methodology was consistent with the Environment Canada reference method, "Standard Reference Method for the Measurement of Suspended Particulate in the Atmosphere (High Volume Method)," EPS Report No. 1-AP-73-2 (January 1983). Sampling periods were of 24 hours duration. This sampling period was perceived to be optimal because of the possibility of PAH losses from filters on longer period sampling due to the volatility of these compounds.^{1,15}

Special handling procedures were involved and this did not allow gravimetric TSP analysis. This special handling involved refrigeration of exposed filters prior to PAH extraction and analysis in order to minimize volatilization of organics off the filter.

Entire filters were run through a Soxhlet extraction and aliquots of the extract were purified and then run on a gas chromatograph. The resultant spectra were compared to standard samples of the six compounds which were prepared and analysed on the same instrument. Elution time was the criterion of identification and peak height was indicative of concentration.

2.1 Monitoring Sites

For this project four monitoring sites were employed. Three were within urban Winnipeg and one was at a rural background station. The three urban locations are part of the Federal Government's National Air Pollution Surveillance (NAPS) network, while the fourth (rural) site is a Provincial monitoring site.

- 1) NAPS Station 9118* - Located at 299 Scotia Street, regarded as representative of an urban residential environment.
- 2) NAPS Station 9119** - Located at 65 Ellen Street, regarded as representative of an urban downtown environment.
- 3) NAPS Station 9210*** - Located at 604 St. Mary's Road, regarded as representative of an urban residential environment.
- 4) Provincial Station 4304 - Located near St. Francois Xavier, regarded as representative of a rural background site.

* In some other departmental publications on air quality this site may be referred to with station number 70118.

** Sometimes referred to as station number 70119.

*** sometimes referred to as station number 70120.

3.0 RESULTS

For the period of monitoring, six samples were collected at each of the four sites plus 5 samples from the 10 μ m size selective sampler co-located at site 9118. Of these 29 samples, which were analyzed for 6 separate PAH compounds (chrysene and triphenylene constitute one test), only one test result was positive being just at the lower analytical detection limit. However, a co-located sample did not yield a positive result.

Tables 1 to 4 summarize the results of sampling at each station, the notation "TR" indicating trace concentration levels appear in the table and reflect low chromatograph peaks which because of their low magnitude can not be regarded, with confidence, as positive results. For each station, a range and mean air volume sample is given. These volumes determine the lower detectable concentration limit.

Table 1 - Results of sampling at Station 9118

Date	Wind Direction	Wind Speed (Knots)	PAH concentrations (ng/m ³)*				
			Fluorene	Phenanthrene	Fluoranthene	Pyrene	Chrysene Typhenylene B[a]p
Feb 02, 1984							
02-24-84	ENE	9	<5.0 (Tr)	<4.4	<3.5 (Tr)	<6.6	<4.6
03-01-84	E	7	<4.9	<4.3 (Tr)	<3.4 (Tr)	<6.4 (Tr)	<4.5 (Tr)
03-07-84	SE	9	<4.7 (Tr)	<4.1 (Tr)	<3.3 (Tr)	<6.1 (Tr)	<4.3 (Tr)
03-13-84	NNE	4	<4.6 (Tr)	<4.1	<3.3 (Tr)	<6.1 (Tr)	4.2
03-19-84	S	9	<5.0 (Tr)	<4.4	<3.5	<6.6	<4.6
03-25-84	SE	8	<5.0 (Tr)	<4.3	<3.5	<6.5	<4.5
							Analyzed
							<21.2

* Air Volume Samples: Range 2054-2218m³ n=6
Mean 2118m³

ng/m³ = nanograms (10⁻⁹ grams) per cubic meter. Values corrected to standard conditions of 25°C and 101.3 kilopascals of pressure.

Tr = Trace (see text)

Table 2 - Results of sampling at Station 9119

Date	Wind Direction	Wind Speed (Knots)	PAH concentrations (ng/m ³)*						Chrysene Typhenylene	B(a)p
			Fluorene	Phenanthrene	Fluoranthene	Pyrene				
02-24-84	ENE	9	<5.2	<4.5 (Tr)	<3.6 (Tr)	<6.8 (Tr)	<4.7	<22.0		
03-01-84	E	7	<5.0 (Tr)	<4.4 (Tr)	<3.5 (Tr)	<6.6 (Tr)	<4.6 (Tr)	21.6		
03-07-84	SE	9	<4.9 (Tr)	<4.3 (Tr)	<3.4 (Tr)	<6.4 (Tr)	<4.5 (Tr)	<21.0		
03-13-84	NNE	4	<4.7 (Tr)	<4.1 (Tr)	<3.3 (Tr)	<6.2 (Tr)	4.3	<20.3		
03-19-84	S	9	<5.1 (Tr)	<4.5 (Tr)	<3.6 (Tr)	<6.7 (Tr)	<4.7	Not		
03-25-84	SE	8	<5.3 (Tr)	<4.6 (Tr)	<3.7	<6.9	<4.8	Analyzed		
								<22.6		

Air Volume Sampled = Range 1952-2173m³ n=6
Mean 2048m³

ng/m³ = nanograms (10⁻⁹ grams) per cubic meter. Values corrected to standard conditions of 25°C and 101.3 kilopascals of pressure.

Tr = Trace (see text)

Table 3 - Results of sampling at Station 9120

Date	Wind Direction	Wind Speed (Knots)	PAH concentrations (ng/m ³) ^a					Chrysene	
			Fluorene	Phenanthrene	Fluoranthene	Pyrene	Typhenylene	B(a)p	
02-24-84	ENE	9	<5.3	<4.6 (Tr)	<3.7 (Tr)	<7.0 (Tr)	<4.8	<22.7	
03-02-84			<12.3	<10.7	<8.6 (Tr)	<16.1 (Tr)	<11.2	52.5	
03-07-84	SE	9	<5.3	<4.6	<3.7 (Tr)	<7.0	<4.8	<22.7	
03-13-84	NNE	4	<5.3	<4.6	<3.7	<6.9	4.8	<22.6	
03-19-84	S	9	<5.4	<4.7	<3.8	<7.1	<4.9	Not	
03-25-84	SE	8	<5.6 (Tr)	<4.9	<3.9	<7.3	<5.1	Analyzed	
								<23.9	

Sampling on 03-02-84 was interrupted and thus short duration. This explains the uncharacteristic values. See max value in parenthesis below.

Air Volume Sampled = Range (890) 1844-1948m³ n=6
Mean 1918m³

ng/m³ = nanograms (10⁻⁹ grams) per cubic meter. Values corrected to standard conditions of 25°C and 101.3 kilopascals of pressure.

Tr = Trace (see text)

Table 4 - Results of sampling at Station 4304

Date	Wind Direction	Wind Speed (Knots)	PAH concentrations (ng/m ³) ^a					
			Fluorene	Phenanthrene	Fluoranthene	Pyrene	Chrysene Typhenylene	Bb/p
02-24-84	ENE	9	<5.1 (Tr)	<4.5	<3.6 (Tr)	<6.7	<4.7	<27.0
03-01-84	E	7	<5.1	<4.5 (Tr)	<3.6 (Tr)	<6.7 (Tr)	<4.7 (Tr)	<21.8
03-07-84	SE	9	<5.2 (Tr)	<4.5 (Tr)	<3.6 (Tr)	<6.8 (Tr)	<4.7	<22.3
03-13-84	NNE	4	<5.1	<4.4	<3.5	<6.6	<4.6	<21.6
03-19-84	S	9	<5.1	<4.5	<3.6	<6.7	<4.7	Not Analyzed
03-25-84	SE	8	<5.3	<4.6	<3.7	<6.9	<4.8	<22.7

Air Volume Sampled = Range 1945-2041m³ n=6
Mean 2000m³

ng/m³ = nanograms (10⁻⁹ grams) per cubic meter. Values corrected to standard conditions of 25°C and 101.3 kilopascals of pressure.

Tr = Trace (see text)

4.0 DISCUSSION OF RESULTS

The minimum detectable mass, on each filter, for specific PAH compounds is constant independent of sampled air volumes.

The minimum detectable mass ($\mu\text{g}/\text{filter}$) for each is:

Fluorene	10.3
Phenanthrene	9.0
Fluoranthene	7.2
Pyrene	13.6
Chrysene and Triphenylene	9.4
Benzo[a]pyrene	44.1

In relation to concentrations in air, the detection limit (ng/m^3) - see Tables 1-4) is inversely proportional to the air volume sampled. As the total volume sampled increases the lower detectable concentration limit for each PAH becomes more sensitive. Thus, the greater the sampled volume of air the lower the minimum detectable concentration. One complication, however, to longer term (hence greater volume) sampling is the volatility of PAH compounds. The degree of volatilization is dependent upon the equilibrium vapour concentration (EVC) of the individual compounds and this may contribute to significant losses, due to sublimation, during storage of all except the most involatile PAH. As mentioned in the Procedures section, 24-hours is about the optimal sampling time using this methodology. Several reports are available in which the question of collection efficiencies (for PAH) of quartz or glass fibre has been addressed.^{1,14,17,18}

The one positive result measured during this survey was at the lower end of the analytical concentration range and was not confirmed by a co-located sample. This observation could be within the accuracy of the sampling/analytical methodology or could represent a contamination of the sample.

Five major factors influence the concentration levels:

Point 1

Actual ambient concentrations may have been below the lower detection limits of our sampling/analysis methodology.

Various PAH compounds have been identified and quantified in urban environments (air) all over the world.¹⁰ While all the specific PAH in this study have not been measured in other studies, one or more have been. Perhaps the most widely monitored compound is benzo[a]pyrene, probably because of its high biological activity (carcinogenicity). Ambient PAH levels have been measured in many U.S. cities, from smaller towns like Petersville Alabama,¹⁹ a residential suburb of Florence, Ala., to large megalopolis areas such as the New York City/Newark N.J. area.^{10,12,20} Studies have also been carried out in other Canadian cities such as Vancouver/Whitehorse²¹ and Sidney N.S.²² Often other studies reveal average levels at or below our calculated lower detection limits (see Tables 1-4). In some cities individual measurements have indicated maximum ambient levels well above our thresholds. This tends to suggest we should have found at least a few positive results. In a project performed in Budapest Hungary, even the minimum measured concentration of 1 of 5 PAH common to both studies (theirs and ours) was above our detection

limit. The maximum measured concentrations of all five common PAH analytes in Budapest were well above our detectable levels, one in particular (chrysene) was 54 times higher at 277 ng per cubic metre.

Point 2

Our high-volume sampling method may be inappropriate for the compounds under investigation.

The sampling methodology used in this study may be inefficient in detecting the presence of PAH. Some of the studies cited in this report have employed the same method and have found positive results. There does, however, seem to be some serious shortcomings involved with this method as reported by other investigators. Pupp et. al. (1974, ref. 14) determined that in using high-volume particulate sampling, measurements of PAH should be considered uncertain by amounts equalling their equilibrium vapour concentration (EVC). They also suggest that collection efficiencies are dependent upon ambient pollutant levels^{14,15,21} and ambient temperatures. Greater losses could be anticipated for the more volatile compounds. Losses for highly volatile, lower weight PAH, such as phenanthrene may be greater than 90% from glass fibre filter media, depending on temperature.^{17,21} Similar losses, up to 90% have been found for benzo[a]pyrene during 24-hour sampling.¹⁸

Point 3

The time (seasonal) or duration (24-hour) of sampling may have been inappropriate.

A common conclusion in other studies is the seasonal variability to PAH levels.^{12,13} Collucci and Begeman (1971;

ref. 10) not only found highest levels in autumn and winter but also determined that levels tended to increase diurnally in the daytime. They suggest that results from U.S. and European cities indicated about a 4:1 ratio generally for winter vs. summer concentrations, especially benzo[a]pyrene. The combustion of various fuels (hydrocarbons) for space-heating increases in Winnipeg in the winter months so it is likely that the highest ambient levels of PAH will occur in winter. The volatility of these compounds will be reduced and potential filter losses minimal during cold weather. Daisey and Lloy (1981, ref. 20) found that there is decreased photodegradation of PAH during winter in New York. This phenomenon would be more pronounced at greater latitudes and would thus, in all likelihood ellicit greater effect in Winnipeg. Associated with this is the finding that high ambient levels of ozone (O_3) tend to promote the degradation of benzo[a]pyrene.¹⁸ Winnipeg customarily experiences lowest average ambient O_3 concentrations in winter. It would seem that our sampling was conducted at the appropriate time of year. As for the duration of sampling, the 24-hour exposure period is not only common but is recommended.¹⁵ Adjustments in sampling time can be made depending on ambient concentrations and in some cases has exceeded 24-hours,²² but even in this case the total volume of air sampled in 72 hours was not greater than ours after 24-hours.

Point 4

The locations for sampling may have been uncharacteristic.

Other studies have indicated that in general ambient urban levels of PAH, in air, exceed rural levels.^{12,13,15,16} This is due

to the fact that total urban emissions of PAH are greater than rural emissions (with the possible exception of forest fires). There is a source to receptor relationship and ambient air concentrations are inversely proportional to the distance from the receptor to the point of emission. For this reason levels in industrial and commercial areas tend to exceed residential levels because of higher emission rates.^{10,12} It has been suggested that the long range transport of atmospheric aerosols may contribute to PAH levels.²⁰

Point 5

The laboratory methods for handling, extraction and analysis of PAH may be inappropriate.

The gas chromatographic method used for the analysis of filter extracts in this study is prescribed for similar investigations. The preparation of standards, of known PAH concentrations is an integral part of the procedure. Given the positive response of the analytical instrument to these standards and the documented PAH recoveries, it is difficult to doubt the efficacy of the method.

5.0 CONCLUSIONS

- 1) With only one positive result from all sampling, the indication is that PAH levels are very low. Most of the PAH are at levels apparently below the detection limits of the analytical instruments used. The representativeness of the sampling methodologies employed, however, is subject to review and potential improvement. This project clearly establishes certain fundamentals for future investigations, but should be regarded as only a preliminary study.
- 2) In the event that subsequent studies are undertaken, improvements in both sampling and analysis procedures should be implemented. Special effort should be directed towards improving the sensitivity of the analytical methods, providing lower detection thresholds, if this could be achieved.

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